Catalytic activation of 3D printed AlSi10Mg Periodic Open Cellular Structures (POCSs) by combined dip/spin coating method for the intensification of ammonia synthesis

Cristina Italiano[1], Assia Saker[2], Massimo Laganà[1], Minju Thomas[1], Benjamin Hary[3], Steve Nardone[3], Nicolas Meynet[2], Lidia Pino[1], Alvaro Ramirez Santos[2], Antonio Vita*[1]

[1] Institute CNR-ITAE, Via Salita S. Lucia sopra Contesse n. 5, 98126 S. Lucia, Messina, Italy
[2] 2ENGIE Lab CRIGEN, 4 Rue Joséphine Baker, Stains, France
[3] ENGIE Laborelec, Rodestraat 125, 1630 Linkebeek, Belgium

Corresponding Author: antonio.vita@itae.cnr.it

ECCE AB 23 — 17 - 21 September 2023, Berlin/Germany

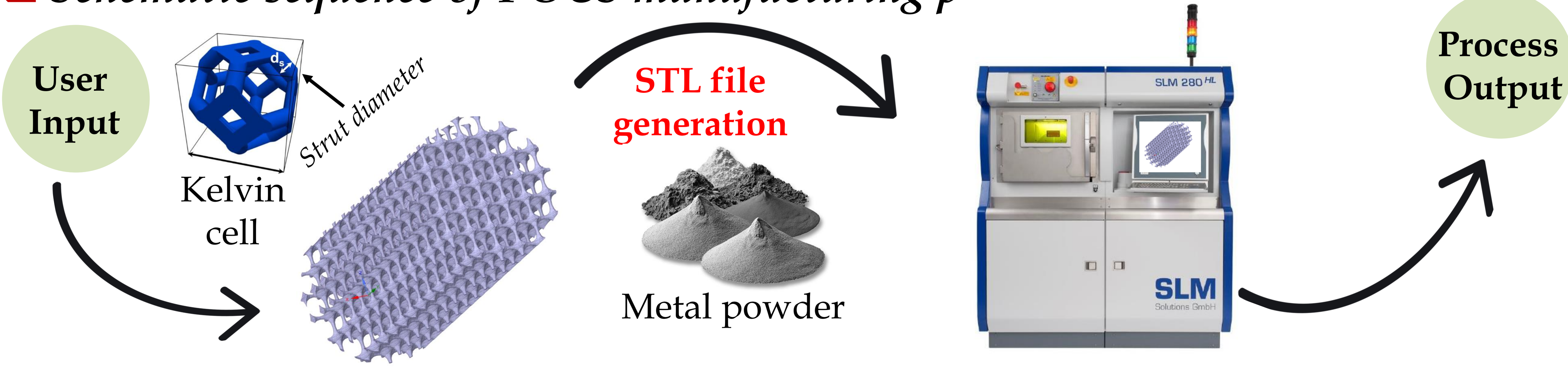
INTRODUCTION

The present work deals with the design, manufacturing (by Laser Powder Bed Fusion), characterization, and catalytic activation (by a wash-coating method) of Periodical Cellular Structures (POCS) 3D-printed in a cylindrical shape (Ø = 1cm, Length = 1.5 cm), in different materials (Al-, Cu-, Ni-alloys) and with various structural parameters (porosity, density, cell type and strut dimensions). The general aim is to intensify the ammonia synthesis throughout the development of structured catalysts with geometries that allow the integration with ammonia selective membranes in a membrane-based reactor to increase productivity at low temperatures (250-300°C) and pressure (20-25bar).

RESULTS

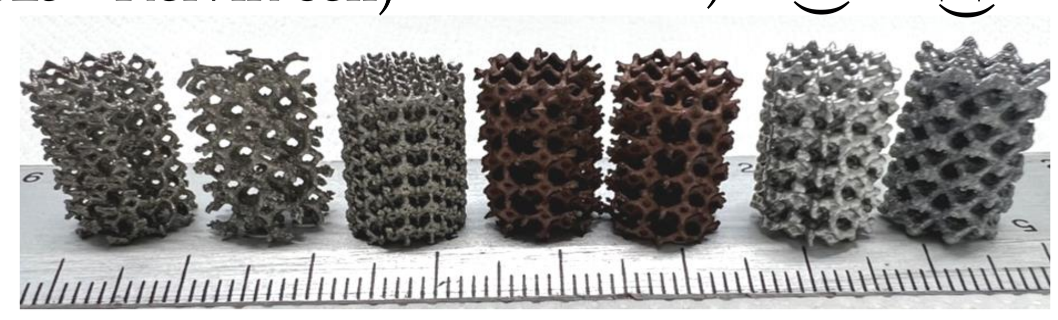
ADDITIVE MANUFACTURING (AM) .... *fast, easy, highly accurate and productive, part of the digital industry..!!*

❑ ***Schematic sequence of POCS manufacturing process***



Final POCS Supports

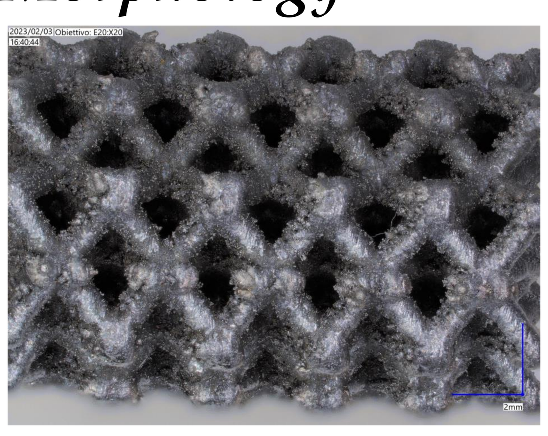
• Ni Alloy (IN625 - Kelvin cell) • Cu Alloy (CuNi2SiCr Kelvin cell) • Al Alloy AlSi10Mg (BCC c.) (Kelvin c.)



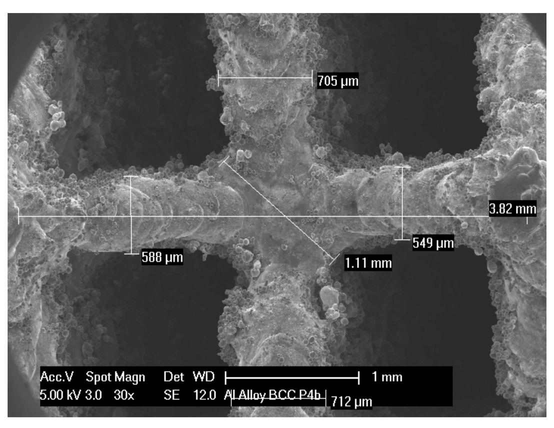
POCS CHARACTERIZATION (AS BUILT)... *complex geometry, high porosity and Specific Surface Area...!!*

❑ ***Morphology***

BCC Al-Alloy

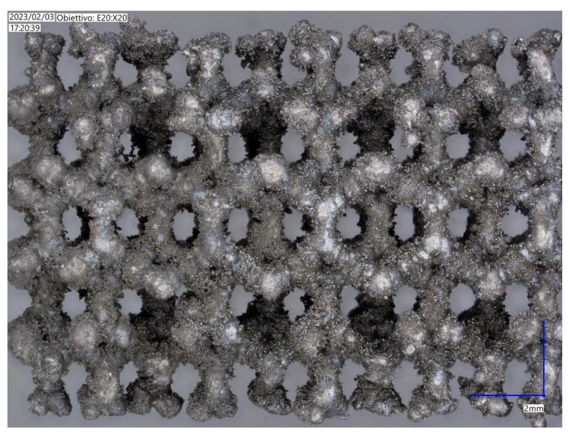


Optical microscope images

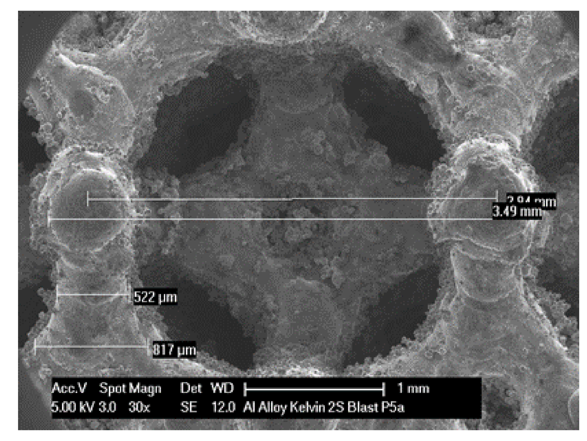


SEM micrograph

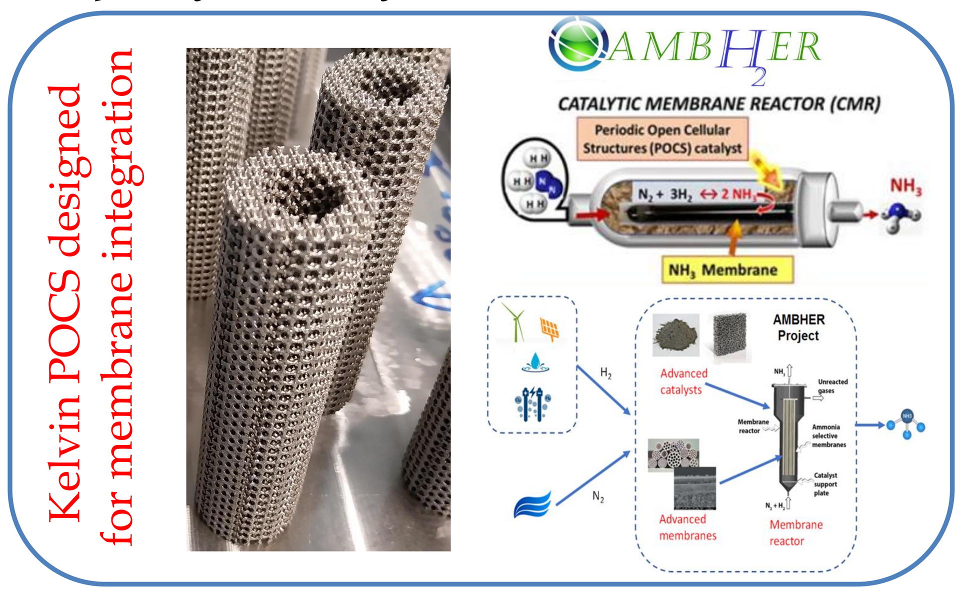
Kelvin Al-Alloy



Optical microscope images



SEM micrograph



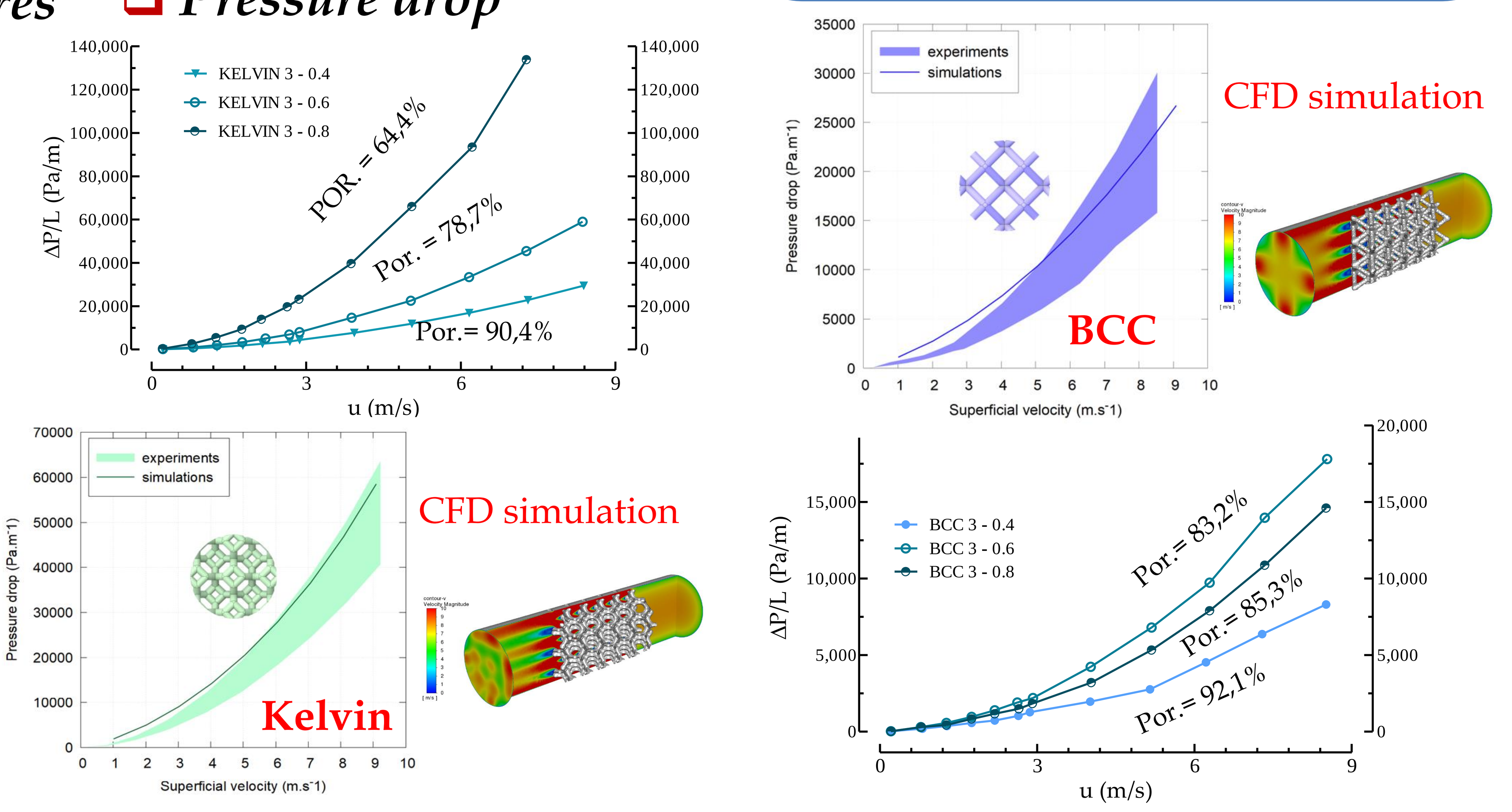
❑ ***Summary of the Ni-alloy POCSs and related geometric features***

Cell type	Cell size (mm)	Strut diameter (mm)	** Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	Geom. density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
BCC	2 (2*)	0.4 (0.41*)	0.219	10.87	9.45	82.9	2.80	87.03	0.17
BCC	2 (2*)	0.6 (0.6*)	0.489	8.79	24.52	63.9	2.02	48.77	0.36
BCC	3 (3*)	0.4 (0.4*)	0.099	11.31	19.06	92.1	3.65	95.66	0.08
BCC	3 (3*)	0.6 (0.59*)	0.220	8.86	23.85	85.3	0.95	58.82	0.17
BCC	4 (4*)	0.6 (0.62*)	0.116	9.14	12.94	91.2	1.48	64.48	0.09
BCC	3 (3*)	0.8 (0.75*)	0.206	16.02	15.41	83.2	0.90	45.85	0.15
BCC	1.5(1.5*)	0.3 (0.3*)	0.212	12.08	7.48	83.3	2.80	115.66	0.17

Cell type	Cell size (mm)	Strut diameter (mm)	** Solid Volume (cm^3)	** Solid density (g/cm^3)	Internal Surface area (cm^2)	** Porosity (%)	Geom. density (g/cm^3)	Specific surf. area (cm^2/cm^3)	Relative density
KELVIN	3 (3.04*)	0.4 (0.44*)	0.126	14.21	11.21	90.4	1.52	88.97	90.4
KELVIN	3 (3*)	0.6 (0.69*)	0.290	10.14	15.23	78.7	2.50	52.52	78.7
KELVIN	3 (3*)	0.8 (0.86*)	0.518	9.42	16.93	64.4	4.14	32.68	64.4
KELVIN	4 (4*)	0.6 (0.61*)	0.153	10.85	9.08	88.6	1.41	59.37	88.6

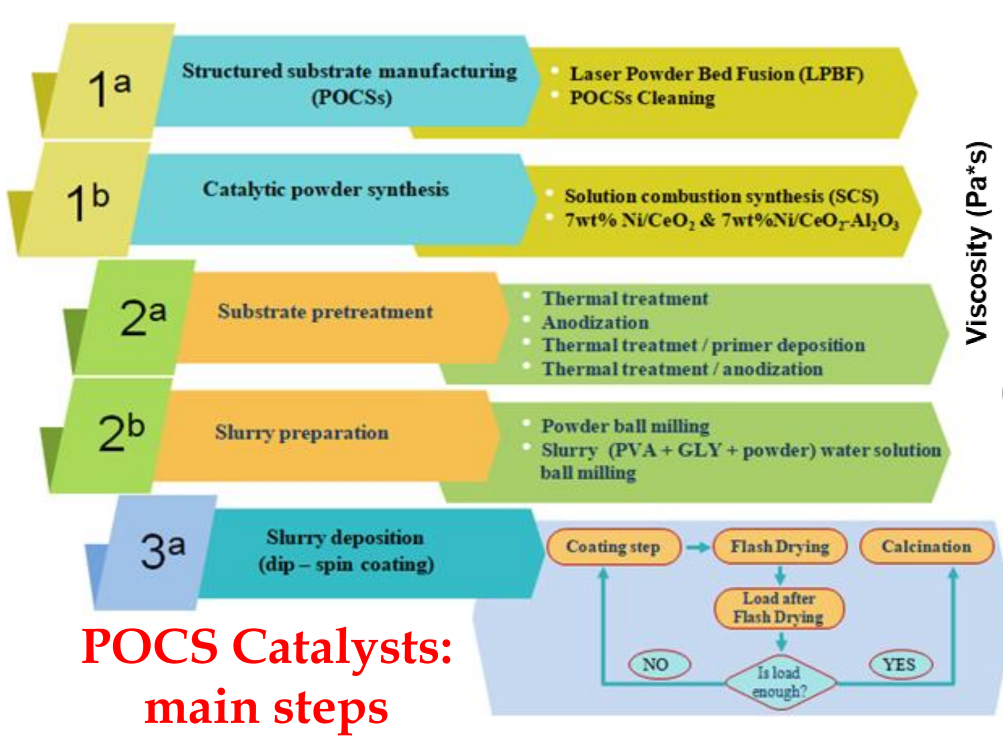
*Calculated from optical images, **Calculated from He pycnometer measurement

❑ ***Pressure drop***

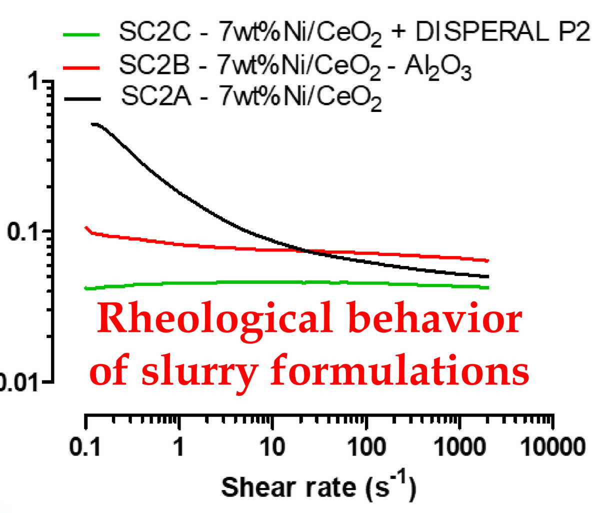


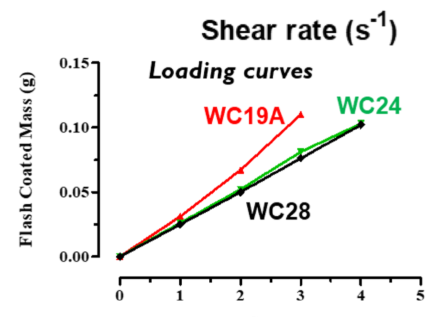
Influence of cell geometry and size, strut diameter and porosity

CATALYTIC ACTIVATION OF POCS… *homogeneous layers, well anchored, no pore-clogging phenomena ..!!*

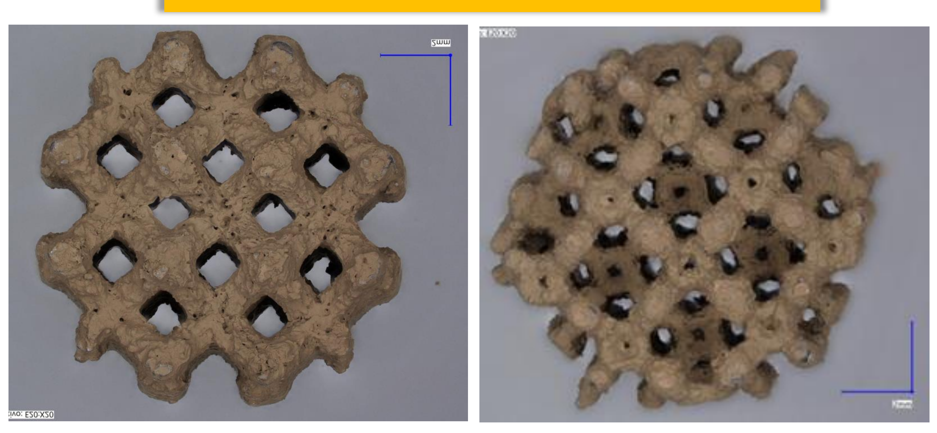


POCS Catalysts: main steps

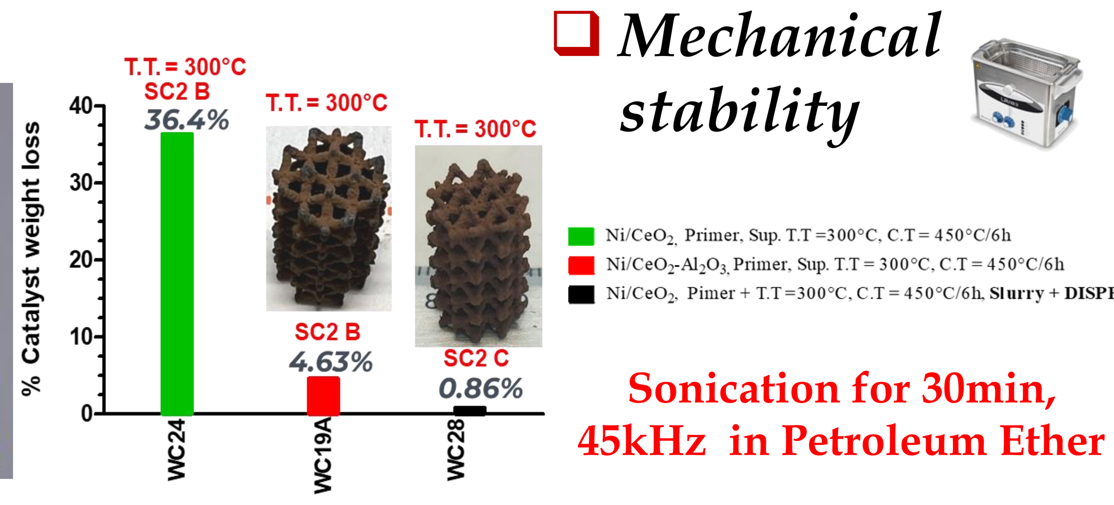




Catalyst loading: 0.1-0.25 g/cm³



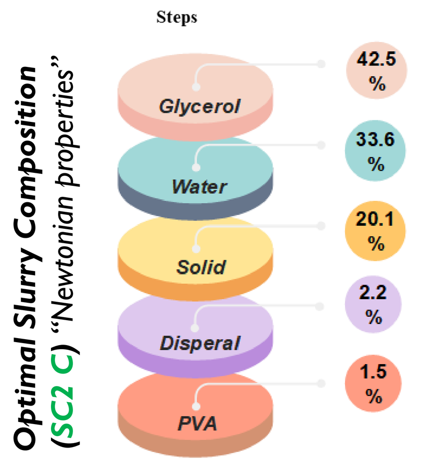
❑ ***Mechanical stability***



Sonication for 30min, 45kHz in Petroleum Ether

Composition of the different slurry prepared.

Slurry	Catalyst formulation	Powder catalyst (%)	Glycerol (%)	PVA (%)	Water (%)	Disperal P2® (%)
SC1	Ni/CeO_2	24.03	45.65	1.49	28.83	-
SC2A	Ni/CeO_2	22.40	42.50	1.50	33.60	-
SC3	Ni/CeO_2	25.36	48.18	1.46	25.00	-
SC2B	Ni/CeO_2-Al_2O_3	22.40	42.50	1.50	33.60	-
SC2C	Ni/CeO_2	20.14	42.50	1.50	33.60	2.26



CONCLUSION

• AM is able to manufacture complex parts allowing more freedom of design optimization for catalytic reactors compared with traditional manufacturing techniques;
• The combined dip/spin coating method can be used to obtain POCS catalysts with homogeneous and stable catalytic layers (thickness ≈ 15µm);
• The presence of anchoring points, the thermal or anodization pre-treatment (or both) of supports or the primer (DISPERAL P2) utilization (both in the slurry and coated on the supports) play a crucial role in achieving high mechanical stability;
• No pore-clogging phenomena were observed irrespective of the geometry used;
• The structured catalytic systems obtained by combining AM with the washcoating technique are characterized by higher porosity (88 -90%), higher SSA (50-115 cm^2/cm^3) and lower pressure drops with respect to the conventional packed bed reactor.

Acknowledgements
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101058565 (Ambher project). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.